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To cite this article: I A Pavlova *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **969** 012030

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The Possibility of Using Tyumen Keramzite Clay in the Production of Ceramic Materials

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Abstract. The properties of red low-melting clay with the aim of its use in the production of building ceramics are investigated. The presented sample of clay raw materials by mineral composition refers to kaolinite clays with mixed-layer formations in the form of illite and ferruginous montmorillonite with Na-, Ca- and Mg-interlayer hydrated exchange cations. It is characterized by an average content of free SiO₂ (10–25%). The clay is medium plastic with a low content of coarse inclusions, it refers to medium raw materials. Clay is medium-drying, medium-sensitive to drying, non-sintering. Mechanical strength during firing at a temperature of 900°C is 27.5 MPa. When firing samples in the temperature range 900–1050°C, a significant black core is formed. At a firing temperature of 1050°C, swelling of the samples occurs. Considering the properties of this clay, it cannot be recommended to produce face and ordinary building bricks. However, the studied clay can be used to produce expanded clay. The introduction of 0.5% of spent technical oil allows to get the expansion coefficient of 3.83. The temperature range of expansion is 1050–1170°C. The density of expanded clay granules in this case is 560 kg·m⁻³.

1. Introduction

Fusible red-burning clays are often overburden or accompanying rocks in mining. Deposits of fusible clays are ubiquitous. The properties of clays of various deposits are not the same and can be used to produce certain types of ceramics [1–5]. Clay properties vary even within the same deposit. Red-burning clays are used on a large scale in the production of building ceramics, and in smaller ones for the production of pottery. Building materials always remain in demand due to the increasing rate of construction in both urban and rural conditions. Fusible clays may be suitable for the production of ceramic bricks, expanded clay, and ceramic tiles. To determine the suitability of clay in the production of a particular type of product, it is necessary to study its ceramic properties and determine the production technology [6–8]. In this regard, research work on determining the suitability of clay in the production of a particular type of product always remains in demand. This project is devoted to the study of the properties of low-melting clay of the Tyumen region in the production of ceramics.

2. Experimental procedure

The chemical composition of the materials is determined according to [9–18]. The content of free SiO₂ in clay was determined according to [19].



Differential thermal analysis was performed by derivatograph (MOM). Heating was carried out in a platinum crucible up to 1000°C with a speed of 10° per min. Al₂O₃ was used as a reference.

Plasticity was tested in accordance with [19]. The plasticity of clay tempered with water is its ability to deform under the influence of a load without breaking the continuity (formation of cracks), take any shape and save it after the removal of the load. The plasticity of clays most of all depends on their disperse and mineral composition. The more dispersed the clay, the higher its plasticity. In ceramic technology, there are many methods for estimation of the plasticity of clays and ceramic masses. All these methods are divided into 2 groups: direct and indirect. Indirect methods cannot simultaneously evaluate the plasticity and molding ability of clays and plastic ceramic masses. As an example of the method of indirect plasticity estimation, the Vasiliev method proposed by [19] is used. When determining clay plasticity using the Vasiliev method, the plasticity number *P* is determined, which is the difference between the relative humidity of the clay at the lower yield strength and the relative humidity of the same clay determined at the plastic limit [20].

The sensitivity of clays to drying was determined by the method of Z. A. Nosova. The sensitivity of clays to drying is their ability or tendency to crack during drying. The cause of cracks is the different shrinkage over the cross section and on the surface of the product. Shrinkage cannot occur evenly for the entire product, as humidity in the surface and in its central zones varies during the drying process. The nonuniformity of shrinkage causes internal local stresses in the material, which can exceed its mechanical strength and cause deformation of the raw material and the formation of cracks. It is the nonuniformity of shrinkage and internal local stresses caused by shrinkage that cause cracking and defects during drying. The coefficient of sensitivity to drying is the ratio of the volumetric shrinkage during drying to the real porosity of the material in the air-dry state. The smaller this coefficient, i.e. the less clay shrinkage during drying, the easier and safer the drying of products. Clays highly sensitive to drying have coefficient of sensitivity of more 1.5; medium-sensitive clays have this index of 1–1.5; insensitive clays have coefficient of sensitivity less than 1.

The ratio of materials to sintering is determined according to [19]. To determine the sintering ability of clay from the mass of optimal molding moisture content (*W* = 18%), cubes of size 50×50×50 mm were formed. Samples are dried and fired at a temperature of 800–1050°C.

3. Results and discussion

Clay samples with a career humidity of 20% in the form of pieces from 5 to 15 cm were ground and dried under room conditions. The color of clay in its raw form is blue-gray. The dried clay was ground on laboratory runners to a grain size of less than 3 mm. The chemical composition of clay is presented in Table 1. According to the content in the clay Al₂O₃ in the calcined state (16.47%), the clay belongs to the semi-acid raw (Al₂O₃ – 28–14%). According to the content of coloring oxides (TiO₂+Fe₂O₃ is 8.85%), clay belongs to clays with a high content of coloring oxides. Clay is characterized by a low content of carbonate inclusions, with a low content of water-soluble salts (1.05 mg·eq per 100 g of clay). The content of free quartz is 25%, which allows to attribute the studied clay to clays with an average content of free quartz (10–25%). The predominant size of quartz particles is from 0.5 to 0.063 mm.

Table 1. The chemical composition of clay.

Oxide	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI
Content in natural clay (%)	61.15	14.80	1.00	7.12	1.62	1.10	1.90	0.84	10.12
Content in calcined matter (%)	68.06	16.47	1.11	7.92	1.80	1.22	2.11	0.93	–

The results of the differential thermal analysis are presented in Figure 1. On the DTA curve, endothermic effects are observed at low temperatures at 136°C, while the loss on ignition is 4.3%. The endothermic effect at 153.4 °C is associated with the removal of interlayer molecular water from illite. A slight bend at 180 °C against the background of the main endothermic effect (on the DTG curve) associated with the removal of water is characteristic of montmorillonite with Ca- and

Mg-interlayer hydrated exchange cations. The next endothermic effect at 394 °C is associated with the release of constitutional water and partial restructuring of the illite structure, while the mass loss is 0.8%. The endothermic effect at 560 °C is associated with the dehydration of kaolinite and the formation of an amorphized metakaolinite phase. Loss on ignition is 4.5%. The exothermic effect at 911 °C is associated with the crystallization of mullite. The total loss on ignition by heating the clay is 10.3%.

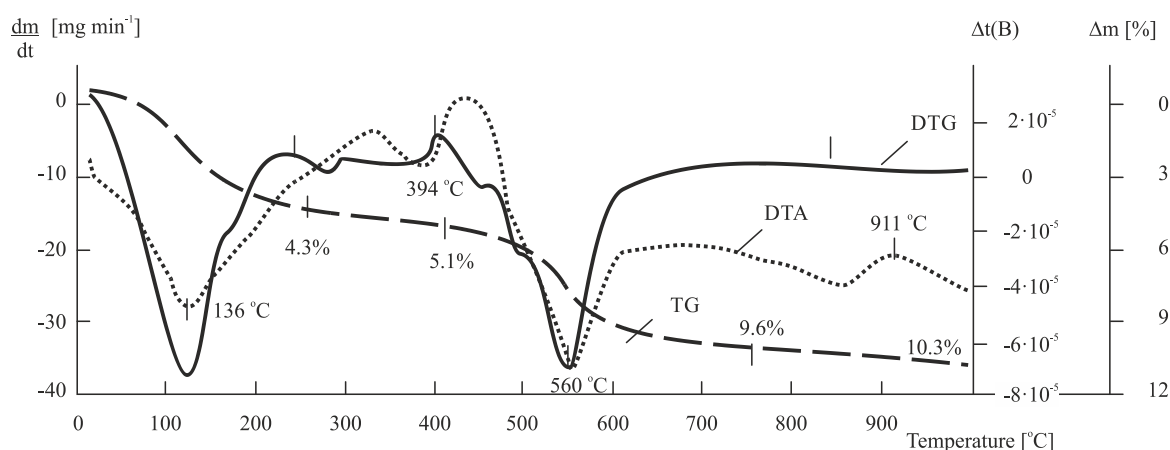


Figure 1. DTA results of clay.

The content of coarse fractions in the clay (particles larger than 0.5 mm) is 0.66%. These are raw materials with a low content of coarse inclusions (less than 1%).

By the size of the predominant coarse inclusions, clay refers to raw materials with small inclusions.

In terms of material composition, inclusions in clay are mainly pyrolusitic with a low content of quartz particles and rare inclusions of limonite.

Fine fractions in clay (Table 2) were determined by the sedimentation method according to [19].

Table 2. The distribution of fine fractions in clay.

Particle size (mm)	> 0.06	0.06–0.01	0.01–0.005	0.005–0.001	< 0.001
Fraction content (%)	8.53	16.39	7.72	13.68	53.68

The total content in the clay of particles less than 10 microns in size is 75.08%, which makes it possible to attribute it to medium-sized raw materials.

The plasticity of clay according to the method of Vasiliev is 22.1. Humidity at the lower yield strength is 35.9%, humidity at the limit of rolling into a tow is 13.8%. The plasticity number of white clay is 22.1. Clay is a medium plastic raw material.

The sensitivity coefficient of clay to drying by the method of Z. A. Nosova is 1.26. This is a medium drying clay. Clay air shrinkage is 7.9%, i.e. clay is medium drying.

To determine the technological properties of clay from the mass of optimal molding moisture content ($W = 19\%$), samples were formed – tiles in size 50×50×10 mm and cubes in size 50×50×50 mm. Samples were dried and calcined at a temperature of 900, 950, 1050 °C. Data on the amount of shrinkage, water absorption, porosity, density and mechanical compressive strength are shown in Table 3.

At a firing temperature of 900 and 950 °C, the clay has a water absorption of 7.1–7.3%. At a firing temperature of 1050 °C, the water absorption is only 2%, but the samples swell. Thus, blue clay is a non-sintering raw material.

At all firing temperatures, clay samples have a significant black core, which is associated with the dispersion of clay (particle content less than 1 μm in size is 53.68%) and the presence in the

clay of a high content of iron oxides and organic substances. The dispersion of clay contributes to the formation of an impermeable crust on the surface of the samples during firing.

Table 3. Sintering degree and mechanical compressive strength of blue clay.

Firing temperature (°C)	Air shrinkage (%)	Fire shrinkage (%)	Total shrinkage (%)	Water absorption (%)	Open porosity (%)	Apparent density (kg·m ⁻³)	Compressive strength (MPa)
900	7.9	1.1	9.0	5.8	11.0	1910	41.9
	7.5	0.8	8.3	5.3	9.7	1840	34.6
	7.4	0.5	7.9	7.1	13.4	1900	54.3
	7.9	1.5	9.4	8.4	16.3	1930	52.2
	7.7	0.8	8.5	8.7	16.7	1920	–
950	7.8	0.3	8.1	7.8	14.8	1.90	30.5
	8.1	0.6	8.7	7.3	13.9	1.90	37.4
	7.7	0.8	8.5	7.2	13.7	1.89	31.9
	8.1	0.4	8.5	7.2	13.6	1.90	–
	8.1	0.7	8.8	7.2	13.5	1.88	–
1050	8.1	3.5	11.6	2.1	4.2	1.95	swollen samples
	8.1	3.6	11.7	2.4	4.7	1.92	
	8.2	3.2	11.4	2.5	4.7	1.88	
	7.7	3.3	11.0	1.4	2.5	1.83	
	7.9	3.7	11.6	1.5	2.7	1.77	

Access of oxygen to the inner layers is limited, while a reducing medium appears inside the samples, which leads to the transition of Fe³⁺ to Fe²⁺. When dispersed organic impurities burn out, sooty carbon forms, which settles in the pores of the products. After drying of water-saturated images of calcined clay, part of the soot goes to the surface of the products, painting them gray. The low gas permeability of the samples during firing also leads to the destruction of some samples, which makes it impossible to obtain not only face, but also ordinary building bricks.

To determine the suitability of clay in the production of expanded clay, a series of samples were made by plastic molding with a molding moisture content of 18–19%. As intumescent component used technical waste oil in an amount of 0.5%. Sample cylinders were molded with a size of 15×15 mm. Dried at room temperature during the day. Heat treatment was carried out at 200°C and fired at a temperature of 1050, 1090, 1130, 1170°C. Samples during firing were installed in a preheated oven to a predetermined temperature. It was kept for 7 min and sharply cooled in air. The average density of the obtained granules and the coefficients of expansion of the mass are given in Table 4.

Table 4. Expanded clay density and expansion coefficient.

Firing temperature (°C)	1050	1090	1130	1170
Average density of granules (kg·m ⁻³)	1280	800	630	560
Expansion coefficient	1,51	2,31	2,85	3,83

The temperature range of expansion is 1050–1170°C with the introduction of technical waste oil. The minimum density of expanded clay samples was obtained by firing at a temperature of 1170°C. Thus, clay is suitable for producing artificial porous aggregates for concrete [20–22]. With the introduction of waste technical oil, the expansion coefficient is up to 3.83.

4. Conclusion

The presented sample of clay raw materials by mineral composition refers to kaolinite clays with mixed-layer formations in the form of illite and ferruginous montmorillonite with Na-, Ca- and Mg-interlayer hydrated exchange cations. It is characterized by an average content of free SiO₂ (10–25%). It is medium plastic, with a low content of coarse inclusions and refers to medium-dispersed raw materials. Clay is medium-drying, medium-sensitive to drying, non-sintering. The mechanical strength during firing of sample cubes at a temperature of 900°C is 27.5 MPa. When firing samples in the temperature range 900–1050°C, a significant black core is formed. At a firing temperature of 1050°C, swelling of the samples occurs. Considering the properties of this clay, it cannot be recommended for obtaining face and ordinary building bricks. However, the studied clay can be used for the production of expanded clay. The introduction of 0.5% of spent technical oil allows to get the expansion coefficient of clay 3.83. The temperature range of expansion is 1050–1170°C, while it is possible to obtain expanded clay with a density of granules of 560 kg·m⁻³.

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